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NITROSAMINE MANUFACTURE

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The present invention relates to a novel process for the preparation of valuable chemical intermediates. The invention relates specifically to a novel process for the preparation of secondary nitrosamines, disubstituted ammonium nitrites, and novel intermediate products by adding nitric oxide to secondary amines. The invention also relates to novel salts and alkylated derivatives of the novel intermediates produced in this process. This application is a continuation-in-part of my co-pending application Serial No. 582,084, filed May 2, 1956, which, in turn, is a continuation-in-part of my application Serial No. 489,275 filed February 18, 1955, both now abandoned.

Nitrosamines, which are useful as insecticides and as chemical intermediates, especially in the preparation of substituted hydrazines, are generally prepared by the nitrosation of a secondary amine by nitrous acid added per se or generated by the reaction of a metal nitrite and a mineral acid. Disubstituted ammonium nitrites, which are known to be especially useful as corrosion inhibitors, are generally prepared by the reaction in aqueous solution of an alkali metal nitrite and a soluble salt of the amine, i.e., the amine hydrochloride. The known processes for the preparation of nitrosamines and disubstituted ammonium nitrites, which obviously are very similar, both have the disadvantage that a worthless and hard-to-remove metal salt is produced as a by-product, and separation of the aqueous phase is necessary. Moreover, the known methods for the preparation of the nitrosamines are not altogether suitable for the preparation of nitrosamines of secondary amines having reactive substituents such as hydroxy, halo, cyano, carbonyl, carboxyl, carboxyalkyl, and nitro groups.

An object of the present invention is to provide an improved process for the nitrosation of amines. Another object of the invention is to provide a simple and inexpensive process for the preparation of nitrosamines and/or disubstituted ammonium nitrites in which the formation of undesirable by-products is avoided. Another object of the invention is to provide a simple and inexpensive process for the preparation of novel addition products of nitric oxide and secondary amines. Additional objects will become apparent as the invention is more fully described.

I have found that the foregoing and related objects are realized by adding nitric oxide to a secondary amine or to a tertiary amine having at least one alkyl group attached to the amino nitrogen. The nitric oxide preferably is added at elevated pressures in order to increase the rate of the reaction. The maximum reaction temperature depends on the decomposition point of the product under the proscribed reaction conditions. The desired products may be obtained by suitable control of the reaction conditions, and no undesirable by-products difficult to remove from the reaction mixture are formed in this process. The use of simple and complex salts of variable-valence metals as catalysts in the present process generally gives

markedly improved results in the yields of product obtained, the rate of reaction, and the like. Suitable salts include the sulfides, halides, cyanides, nitrates, and pyridinium chlorides of manganese, chromium, cobalt, nickel, tin, iron, and copper, as well as the nitric oxide complexes of the salts of these metals. The nitric oxide complexes are readily formed in situ under the conditions of my process. Supported nickel, palladium, and rhodium catalysts likewise generally improve the yields and accelerate the reaction in the present process, carbon-supported palladium being particularly effective.

Nitric oxide may be added during the course of the reaction to replace that consumed in the reaction. By nitric oxide in the present specification and claims is meant gaseous NO substantially free of higher oxides of nitrogen or other reactive gases such as oxygen. However, the nitric oxide may be diluted by a gas which does not participate in the reaction, for example, nitrogen or steam, to moderate the reaction. Ammonia oxidation gases may be used, provided that these gases are substantially free of higher oxides of nitrogen. The excess gas may be recovered by conventional means.

The process can be carried out batchwise or continously. Since the products obtained depend on the reaction conditions, the following examples are given to illustrate specific embodiments of the method of carrying out the present invention. Parts are by weight unless otherwise specified. Conversions are based on the amine used as starting material.

Example 1

An autoclave containing 34 parts of dimethylamine and 1.0 part of cupric chloride was pressurized to 270 p.s.i.ga. with nitric oxide. A maximum temperature of 97° C. was attained. When the pressure in the autoclave decreased, additional nitric oxide was added intermittently to raise the pressure to the initial level. At the end of 5 hours, the autoclave was cooled and vented. Distillation of the reaction product yielded 40 parts (71% conversion and yield) of dimethylnitrosamine. Similar yields of dimethylnitrosamine are obtained in the reaction of the amine and nitric oxide when the cupric chloride is replaced by a small amount of 10% palladium-on-charcoal. In this case, no external heating is needed and the reaction preferably is effected in a solvent medium, e.g., methanol or 95% ethanol.

When a mixture of 34 parts of dimethylamine and 50 parts of water was treated with nitric oxide at 235 p.s.i.ga. and 93° C. for 4 hours, and the reaction mixture was extracted with ether, evaporation of the ether extract yielded 2.5 parts (4.5/ conversion) of dimethylnitrosamine.

Example 2

An autoclave containing 35 parts of diethylamine was pressurized to 300 p.s.i.ga. with nitric oxide. A maximum temperature of 104° C. was attained. When the pressure in the autoclave decreased, additional nitric oxide was added to raise the pressure to the initial level. At the end of 4 hours, the autoclave was cooled and vented. Distillation of the reaction product yielded 3 parts of unreacted diethylamine and 32 parts (64% conversion, 70% yield) of diethylnitrosamine.

Example 3

An autoclave containing 20 parts of triethylamine and 2 parts of ferrous sulfide was pressurized to 300 p.s.i.ga.